

The University of Chicago

RELATIVE INTENSITIES IN
THE PRINCIPAL DOUBLET OF THALLIUM
UNDER ARC AND FLUORESCENCE
EXCITATION

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1936

By

LAWRENCE NORTON MORSCHER, JR.

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
THE PHYSICAL REVIEW
Vol. 48, No. 5, September 1, 1935

The University of Chicago

RELATIVE INTENSITIES IN
THE PRINCIPAL DOUBLET OF THALLIUM
UNDER ARC AND FLUORESCENCE
EXCITATION

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1936

By

LAWRENCE NORTON MORSCHER, JR.

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
THE PHYSICAL REVIEW
Vol. 48, No. 5, September 1, 1935



Relative Intensities in the Principal Doublet of Thallium Under Arc and Fluorescence Excitation

L. N. MORSCHER, JR., *Ryerson Physical Laboratory, University of Chicago*

(Received May 23, 1935)

In harmony with theory, the components of the thallium resonance doublet ($6^2P_{1/2, 3/2} - 7^2S_{1/2}$) were found to have approximately the same relative intensities under arc and fluorescence excitations. The average value found for the ratio is 0.92, the violet line being the stronger.

INTRODUCTION

EINSTEIN'S quantum analysis¹ of the radiation from excited atoms has been very generally accepted as valid. Since its formulation it has been a part of quantum theory, sometimes being viewed as an assumption, sometimes as derived.² A laboratory experiment which focuses sharply on this particular analysis seems hard to find and its experimental proof is not clearly distinguishable from the verification of a large body of quantum theory.

A direct consequence of Einstein's theory which seems adapted to a ready experimental proof is the well-known one that the relative intensities of lines with the same initial state should be independent of the conditions of excitation whenever forced transitions can be neglected. This rests directly on his assumption that the intensity due to spontaneous transitions is equal to the product of the number of atoms in the upper state (population) multiplied by a transition probability depending only on the states involved. Recently this consequence of the theory has been challenged on the basis of experimental evidence, notably by Christensen and Rollefson³ and by Berry and Rollefson.⁴ They conclude by indirect measurements that for excitation by fluorescence, the intensity ratio of the $2S-3P$ and $1S-3P$ unresolved sodium lines is about 2 : 1. This they compare

with the value 25 : 1 found by Weiss⁵ in a direct measurement of this ratio in a low voltage arc. In a theoretical paper, however, Prokofjew⁶ estimates this ratio to be 2.1 : 1 and shows that Weiss' value of 25 : 1 clashes with the Thomas-Kuhn sum rules. Hence it seems quite possible that the disagreement with Einstein's assumption is due to an error in Weiss' measurements. The purpose of the present paper is to present the results of a more direct experimental test which is free from possible effects of fine structure.⁷

Pairs of spectral lines with a common upper state which are not too far apart nor too close together and which can be conveniently used in fluorescence work are difficult to find. A suitable pair is the principal doublet of thallium, which has been chosen for the experiments reported here. The relative intensities of the components have been directly measured for excitation by radiation (fluorescence) and by arc. However, even in this case we do not have a situation in which Einstein's assumption can be completely isolated from other assumptions of quantum theory. Self-absorption and forced transitions as well as splitting due to hyperfine structure and stray fields give rise to the chief departures from the idealized case. The influence of absorption is allowed for, that of forced transitions neglected as small. The effect of the multiplicity of states is treated theoretically in the next paragraph.

¹ A. Einstein, *Verh. d. Deutsch. physik. Ges.* **18**, 318 (1916); *Physik. Zeits.* **18**, 1921 (1917).

² An early formulation of Schrödinger which held the unusual position of running counter to this general scheme, was refuted by Gaviola, *Nature* **122**, 772 (1928). The scheme was first derived by P. A. M. Dirac, *Proc. Roy. Soc. A* **114**, 243 (1927). In earlier theories it was wholly or partly assumed.

³ C. J. Christensen and G. K. Rollefson, *Phys. Rev.* **34**, 1157 (1929).

⁴ N. E. Berry and G. K. Rollefson, *Phys. Rev.* **38**, 1599 (1931).

⁵ C. Weiss, *Ann. d. Physik* **1**, 565 (1929).

⁶ W. K. Prokofjew, *Zeits. f. Physik* **58**, 255 (1929).

⁷ The writer is indebted to Professor Mulliken for calling his attention to papers by J. Kaplan which claim that there are intensity anomalies in band spectra indicating variably transition coefficients. See J. Kaplan, *Phys. Rev.* **36**, 778 (1930); **37**, 1406 (1931); **38**, 373 (1931); **38**, 582 (1931); **38**, 1079 (1931); **39**, 180 (1932); **41**, 114 (1932); **42**, 86 (1932). H. Schüler and J. E. Keyston, *Zeits. f. Physik* **71**, 413 (1931) report hyperfine structure intensity anomalies which challenge Einstein's theory.

On the basis of a quantum mechanical vector model of the atom, one may derive the usual sum rules for dipole transition probabilities.⁸ In case of the principal thallium doublet, the hyperfine structure intervals are small compared with the fine structure intervals and we may expect the sum rules to hold rather well for those components of each line due to hyperfine structure and to stray field splittings. Consequently the probability of a transition from any particular component of $7^2S_{1/2}$ to the $6^2P_{1/2}$ levels should be the same as for any other component, likewise for the $7^2S_{1/2}$ to $6^2P_{3/2}$ transitions. Hence the relative doublet intensities should be practically independent of the way in which the population is partitioned among the $7^2S_{1/2}$ levels, and therefore independent of the type of excitation.⁹ It ought to be clear that the results of the present experiment do not test just Einstein's scheme but rather a larger body of assumptions including that scheme.

EXPERIMENTAL PROCEDURE AND RESULTS

The exciting source used in the fluorescence work consisted of a helium arc containing pieces of thallium in a Lavite constriction. Allowance for absorption in the thallium vapor was made on the assumption that the same absorption coefficient was good for all parts of a line.¹⁰ The arc source, following Vonwiller,¹¹ consisted of an upper copper cathode and a lower lead-thallium anode.

Intensity measurements were made photo-

graphically¹² using a tungsten filament as the standard source. In the case of the three-hour exposures used in the fluorescence study, weakening was accomplished by the use of rocking screens¹³ and a photographic step weakener; in putting the comparison strips on two minute exposure arc plates, both step weakener and varying slit methods were used, yielding substantially the same results. A glass filter was employed to render the blackenings of the two lines approximately equal. (A potassium ferrocyanide filter as used by Vonwiller¹¹ was tried but found to decompose.)

Measurements of five plates taken in the arc study gave 0.99, 0.86, 0.89, 0.96, 0.91 averaging 0.92 for the $P_{3/2}-S_{1/2}$ to $P_{1/2}-S_{1/2}$ intensity ratio. Three plates taken in the fluorescence work gave 0.98, 0.95, 0.84, averaging 0.92.

In appraising the above data it should be remembered that the determinations of this ratio in the arc and fluorescence cases were based upon the same calibrations and measuring methods and hence have a comparative significance apart from their absolute value. The intensity ratio of 0.92 diverges considerably from Vonwiller's arc value of 0.64.¹¹ The present experiment indicates, in conformity with theory, that arc and fluorescence excitation lead to approximately the same intensity ratio for the principal thallium doublet.

The writer wishes to thank Professor F. C. Hoyt for suggesting this problem and to thank him and Professor G. S. Monk for directing the research. The author is also indebted to Dr. F. P. Zscheile of the chemistry department, to Dr. A. E. Shaw of the physics department and to Mr. I. Kalberg.

⁸ P. Güttinger and W. Pauli, *Zeits. f. Physik* **67**, 743 (1931); H. C. Brinkman, *Zur Quantenmechanik der Multipolestrahlung*, P. Noordhoff N.V. (1932).

⁹ Since the above argument is applicable to each of the almost identical isotopes of thallium, the presence of several atomic species should not invalidate the conclusions.

¹⁰ For details of procedure see reference 3. For criticism of method see reference 4.

¹¹ O. U. Vonwiller, *Phys. Rev.* **35**, 802 (1930).

¹² G. R. Harrison, *J. Opt. Soc. Am. and Rev. Sci. Inst.* **19**, 267 (1929).

¹³ G. R. Harrison, *J. Opt. Soc. Am. and Rev. Sci. Inst.* **18**, 492 (1929).

